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TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371ATTORNEY'S DOCKET NUMBER
33808F172U.S. APPLICATION NO (if known,
see 37 CFR 1.5)

10/088738

INTERNATIONAL APPLICATION NO
PCT/FR00/02583 ✓INTERNATIONAL FILING DATE
September 18, 2000 ✓PRIORITY DATE CLAIMED
September 24, 1999 ✓TITLE OF INVENTION
APPLICANT(S) FOR DO/EO/USREDUCTION OF THE COKING IN CRACKING REACTORS
Francis Humblot, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

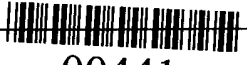
1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau) (see below 16e).
 - b. ☒ has been transmitted by the International Bureau (see accompanying PCT Form 308).
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 34 (35 U.S.C. 371).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 34 (35 U.S.C. 371).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter
16. ☒ Other items or information
 - a. PCT Publication WO 01/21731 with International Search Report (PCT/ISA/210)
 - b. PCT Request (Form PCT/RO/101)
 - c. Notice Informing the Applicant of the Communication of the International Application to the Designated Offices (PCT/IB/308)
 - d. Form PCT/ISA/220 (in French)
 - e. International Search Report (Form PCT/ISA/210 (in French))
 - f. Form PCT/IB/332 (in French)
 - g. International Preliminary Examination Report (Form PCT/IPEA/409 and PCT/IPEA/416) (in French)
 - h.

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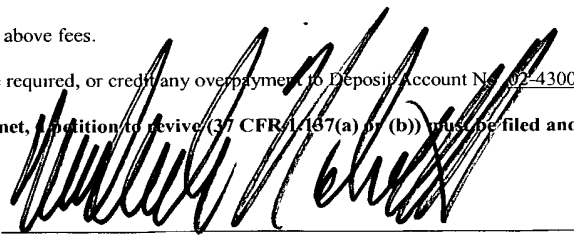
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. . . . \$ 1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.495(e))				\$ ---	
Claims	Number Filed	Number Extra	Rate		
Total Claims	24 - 20 =	4	x \$18.00	72.00	
Independent Claims	1 - 3 =	0	x \$84.00		
Multiple dependent claim(s) (if applicable)			+ \$280.00		
TOTAL OF ABOVE CALCULATIONS =				\$ 962.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).					
SUBTOTAL =				\$ 962.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f))				+	---
TOTAL NATIONAL FEE =				\$ 962.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property.				+	
TOTAL FEES ENCLOSED =				\$962.00	
 00441 PATENT TRADEMARK OFFICE				Amount to be refunded	\$
				charged	\$

- a. ☒ A check in the amount of \$962.00 to cover the above fees is enclosed
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$_____ to cover the above fees.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4300

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.187(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

SMITH, GAMBRELL & RUSSELL, LLP
 1850 M Street, N.W., Suite 800
 Washington, D.C. 20036
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 SIGNATURE

Frederick F. Calvetti 28,557
 NAME REGISTRATION NO.
 Date: March 22, 2002

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PATENT

--Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims. The foregoing references are hereby incorporated by reference.--

IN THE CLAIMS:

Applicants have attached to this Amendment documents entitled "Amended Claims" and "Marked-Up Copy of Previous Claims". Please replace claims 1-18 with amended claims 1-18 as shown in the document entitled "Amended Claims". Please add new claims 19-24 as shown in the document entitled "Amended Claims".

REMARKS

Entry and consideration of this Preliminary Amendment are respectfully requested prior to or concurrent with calculation of the filing fees. This Preliminary Amendment is being filed to correct multiple dependency claims and to avoid the multiple dependency fee. As so amended, the claims are submitted as appearing in proper form.

Examination on the merits is awaited.

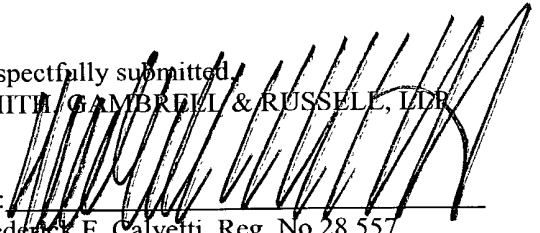
AUTHORIZATION

No additional fee is believed to be necessary.

The Commissioner is hereby authorized to charge any additional fees, which may be required for this amendment, or credit any overpayment to Deposit Account No. 02-4300, Order No. 33808.172.

In the event that an extension of time is required, or which may be required in addition to that requested in a petition for an extension of time, the Commissioner is requested to grant a petition for that extension of time which is required to make this response timely and is hereby authorized to charge any fee for such an extension of time or credit any overpayment for an extension of time to Deposit Account No. 02-4300, Order No. 33808.172.

Respectfully submitted,
SMITH, GAMBRELL & RUSSELL, LLP

By: 
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March 22, 2002

$$\frac{\partial \mathcal{H}}{\partial \mathbf{a}_i} = \left[\frac{\partial \mathcal{H}}{\partial \mathbf{a}_i} \right]_{\mathbf{a}_i = \mathbf{a}_i^*} + \left[\frac{\partial \mathcal{H}}{\partial \mathbf{a}_i} \right]_{\mathbf{a}_i = \mathbf{a}_i^*}^T \mathbf{a}_i^* + \frac{1}{2} \left[\frac{\partial^2 \mathcal{H}}{\partial \mathbf{a}_i^2} \right]_{\mathbf{a}_i = \mathbf{a}_i^*} \mathbf{a}_i^* \mathbf{a}_i^{*T} + \frac{1}{6} \left[\frac{\partial^3 \mathcal{H}}{\partial \mathbf{a}_i^3} \right]_{\mathbf{a}_i = \mathbf{a}_i^*} \mathbf{a}_i^* \mathbf{a}_i^* \mathbf{a}_i^{*T} + \frac{1}{24} \left[\frac{\partial^4 \mathcal{H}}{\partial \mathbf{a}_i^4} \right]_{\mathbf{a}_i = \mathbf{a}_i^*} \mathbf{a}_i^* \mathbf{a}_i^* \mathbf{a}_i^* \mathbf{a}_i^{*T} + \dots$$

MARKED UP COPY OF CLAIMS

1. (Amended) Process for reducing the coking on the metal walls of a reactor for the cracking of hydrocarbons or of other organic compounds and on the metal walls of a heat exchanger placed subsequent to the cracking reactor, [characterized in that] comprising the metal surfaces coming into contact with the organic substance to be cracked are pretreated with a stream of steam comprising at least one silicon compound and at least one sulphur compound at a temperature of between 300 and 1100°C for a time of 0.5 to 12 hours.

2. (Amended) Process according to Claim 1, [in which] wherein the pretreatment of the cracking reactor is carried out at a temperature of between 750 and 1050°C.

3. (Amended) Process according to Claim 1 [or 2], [in which] wherein the pretreatment of the heat exchanger placed subsequent to the cracking reactor is carried out at a temperature of between 400 and 700°C.

4. (Amended) Process according to [one of Claims 1 to 3, in which] Claim 1, wherein the pretreatment is carried out for a time of 1 to 6 hours.

5. (Amended) Process according to [one of Claims 1 to 4, in which] Claim 1, wherein the steam used as carrier fluid additionally comprises an inert gas.

6. (Amended) Process according to [one of Claims 1 to 5, in which] Claim 1, wherein use is made, as silyl compound, of a compound comprising only silicon, carbon, hydrogen and, optionally, oxygen.

7. (Amended) Process according to Claim 6, [in which] wherein the silyl compound is hexamethyldisiloxane.

8. (Amended) Process according to [one of Claims 1 to 7, in which] Claim 1, wherein use is made, as sulphur compound, of carbon disulphide or a compound of [general] formula $R^1-S_x-R^2$ in which R^1 and R^2 , which are identical or different, each represent a hydrogen atom or a hydrocarbonaceous group and x is a number equal to or greater than 1.

9. (Amended) Process according to Claim 8, [in which] wherein the sulphur compound is dimethyl disulphide.

10. (Amended) Process according to [one of Claims 1 to 9, in which] Claim 1, wherein the Si:S atomic ratio is between 5:1 and 1:5[, preferably between 2:1 and 1:2].

11. (Amended) Process according to [one of Claims 1 to 10, in which] Claim 1, wherein the concentration by mass of sulphur and silyl additives in the carrier fluid is between 50 and 5000 ppm[, preferably between 100 and 3000 ppm].

12. (Amended) Process according to [one of Claims 1 to 11, in which] Claim 1, wherein the pressure varies between 1 and 20 bar absolute[, preferably between 1 and 5 bar absolute].

13. (Amended) Process according to [one of Claims 1 to 12, in which,] Claim 1, wherein after the pretreatment, a sulphur compound and/or a silyl compound are added to the feedstock of the organic compound to be cracked.

14. (Amended) Process according to Claim 13, [in which] wherein the sulphur compound is dimethyl disulphide.

15. (Amended) Process according to Claim 13 [or 14, in which] wherein the silyl compound is hexamethyldisiloxane.

16. (Amended) Process according to [one of Claims 13 to 15, in which] Claim 13, wherein the Si:S atomic ratio does not exceed 2:1 [and is preferably less than or equal to 1:2].

17. (Amended) Process according to [one of Claims 13 to 15, in which] Claim 13, wherein there is added, to a feedstock of organic compound to be cracked comprising sulphur, a silyl compound in an amount such that the Si:S atomic ratio does not exceed 2:1, [preferably of less than or equal to 1:2,] and that the concentration of silicon does not exceed 500 ppm.

18. (Amended) Process according to [one of Claims 13 to 17, in which] Claim 13, wherein the concentration by mass of sulphur in the organic compound to be cracked is between 10 and 1000 ppm[, preferably between 20 and 300 ppm].

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AMENDED CLAIMS

2. (Amended) Process according to Claim 1, wherein the pretreatment of the cracking reactor is carried out at a temperature of between 750 and 1050°C.

3. (Amended) Process according to Claim 1, wherein the pretreatment of the heat exchanger placed subsequent to the cracking reactor is carried out at a temperature of between 400 and 700°C.

4. (Amended) Process according to Claim 1, wherein the pretreatment is carried out for a time of 1 to 6 hours.

5. (Amended) Process according to Claim 1, wherein the steam used as carrier fluid additionally comprises an inert gas.

6. (Amended) Process according to Claim 1, wherein use is made, as silyl compound, of a compound comprising only silicon, carbon, hydrogen and, optionally, oxygen.

7. (Amended) Process according to Claim 6, wherein the silyl compound is hexamethyldisiloxane.

8. (Amended) Process according to Claim 1, wherein use is made, as sulphur compound, of carbon disulphide or a compound of formula $R^1-S_x-R^2$ in which R^1 and R^2 , which are identical or different, each represent a hydrogen atom or a hydrocarbonaceous group and x is a number equal to or greater than 1.

9. (Amended) Process according to Claim 8, wherein the sulphur compound is dimethyl disulphide.

10. (Amended) Process according to Claim 1, wherein the Si:S atomic ratio is between 5:1 and 1:5.

11. (Amended) Process according to Claim 1, wherein the concentration by mass of sulphur and silyl additives in the carrier fluid is between 50 and 5000 ppm.

WO 01/21731

PCT/FR00/02583

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REDUCTION OF THE COKING IN CRACKING REACTORS

The present invention relates to the field of the cracking of hydrocarbons or other organic compounds and has more particularly as subject-matter a process
5 for reducing the coking on the walls of the cracking reactors and of the heat exchangers used to cool the compounds resulting from the cracking reaction.

In order to produce ethylene and other short-chain olefins, some hydrocarbon petroleum cuts are
10 thermally cracked in metal tubular reactors. The resulting cracking gases are suddenly cooled in heat exchangers operating with a pressurized steam and water supply.

The tubular reactors used are preferably
15 manufactured from chromium- and nickel-rich steels, whereas the heat exchangers, subjected to less severe constraints, are made of carbon steels. This same type of equipment is also encountered in producing other organic compounds, such as vinyl chloride by pyrolysis
20 of 1,2-dichloroethane.

The efficiency of these steel reactors and heat exchangers depends on their resistance to the formation of a coke deposit on their internal walls in contact with the hydrocarbon to be cracked. Not only is
25 this deposit harmful to the heat transfer but it reduces the effective cross section of the tube. The thickness of this coke deposit becomes such that the

unit has to be shut down and subjected to expensive cleaning operations. In the majority of cases, the coke deposit is removed by high temperature gasification with a mixture of steam and air, which converts the
5 coke to carbon oxides and re-establishes the initial characteristics of the cracking tube. When the deposit is produced in the heat exchangers, it is not possible structurally to carry out an in line decoking by gasification as the maximum temperatures allowable are
10 too low for this reaction to be possible. Dismantling and decoking under manual conditions is necessary, a lengthy and difficult operation.

Despite optimized procedures which completely remove the coke, hydrocarbon cracking units, such as
15 steam crackers, are frequently shut down in order to be subjected to fresh decoking cycles (after operating for 20 to 60 days). Furthermore, the oxidizing decoking treatment results in an increase in the catalytic activity of the metal cracking surface, which increases
20 the rate of formation of coke. Thus, with the increase in the number of decoking operations to which the unit is subjected, the operating time decreases and the annual number of decoking operation increases. This long-term effect is technically and economically
25 harmful since the maintenance costs become increasingly burdensome with the age of the unit for a lower annual operating rate.

For this reason, numerous efforts have been made over the years to find solutions which prevent the rapid coking of the internal metal walls of such units (cracking tubes and heat exchangers). Mention may more particularly be made, among the numerous solutions described in the literature, of the following:

1) A first method, disclosed in Patent US 4,099,990 and a subsequent publication by D.E. Brown et al. in ACS Symp. Ser. 202 (1982) 23, consists in forming, from alkyloxysilane, a silica coating by thermal decomposition in the vapour phase. A degree of improvement in the quality of the deposit can be obtained by using a silicone oil under specific conditions (Chem. Techn. (Leipzig) 42 (1990) 146). However, the process is rather expensive and the silica layer is not very stable beyond 750°C, a standard temperature for the cracking tubes of industrial plants.

2) Patent US 4,410,418 discloses a method for depositing a silica film from halosilane. The silyl compound is deposited liquid, as a film, on the metal surface to be treated and then, by exposure to moisture, a silica layer is formed by hydrolysis. This technique is difficult to apply to industrial plants because it is complicated to carry out; in addition, it is accompanied by a release of acids which can corrode the metal walls.

3) In Patents EP 540,084, EP 654,544 and EP 671,483, a protective layer of ceramic type is obtained from silyl compounds which do not comprise alkoxy groups and which are cracked in the presence of steam or of inert gas.

4) Patents US 4,692,243, US 5,565,087, US 5,616,236, US 5,656,150, EP 698,652 and EP 770,665 all relate to a method for reducing the formation of coke in a hydrocarbon cracking tube. This method employs a silicon compound as a mixture with a tin compound. Some improvements have been made to it, such as the use of a reducing gas as carrier fluid for pretreating the cracking tube (Patent US 5,616,236) or the cracking of a desulphurized feedstock (Patent EP 770,665). This type of treatment remains expensive and the long-term effects of the tin on the metallurgy of the cracking tube and in the downstream sections are not known.

5) Patent US 5,849,176 discloses a process in which an additive composed of sulphur and of silicon is added to the feedstock of the cracking unit. The formation of coke is reduced to a greater extent than with a silyl compound alone or a sulphur compound alone. This patent claims the use of compounds based on sulphur and on silicon for reducing the coking in the cracking tubes and also in the heat exchangers placed in line subsequent to the cracking reactor. The amounts

of silicon thus introduced end up being not insignificant and there is reason to fear blockages either in the cracking tube or in the section for treatment of the cracked gases.

5 6) Patent Application WO 95/22588 claims a process in which the cracking tube is pretreated in an inert gas (nitrogen, methane, hydrogen) with an additive based on sulphur and on silicon. A significant reduction in the amount of coke formed during the
10 cracking of the hydrocarbonaceous feedstock is obtained. A true synergy exists between the sulphur and the silicon since no additive based on sulphur or on silicon alone leads to such results. However, the use of an inert carrier gas seems to be essential to this
15 performance. Example 6 and Figure 7 of this patent application show that the use of steam as carrier gas with an additive composed of trimethylsilylmethyl mercaptan does not result in any inhibition of the formation of coke.

20 Surprisingly, it has now been found that an additive composed of a mixture of sulphur compound and of silyl compound can be used to pretreat a hydrocarbon cracking tube in steam and thus to significantly reduce the formation of coke which accompanies the hydrocarbon
25 cracking reaction.

By comparison with the process disclosed in Patent Application WO 95/22588, this novel process is

easier to install in steam cracking units since, as carrier gas, it uses steam, a fluid already ordinarily available in the said units.

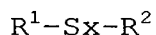
A first subject-matter of the invention is
5 thus a process for reducing the coking on the metal walls of a reactor for the cracking of hydrocarbons or of other organic compounds and on the metal walls of a heat exchanger placed subsequent to the cracking reactor, characterized in that the metal surfaces
10 coming into contact with the organic substance to be cracked are pretreated with a stream of steam comprising at least one silicon compound and at least one sulphur compound at a temperature of between 300 and 1100°C, preferably between 400 and 700°C for the
15 heat exchanger and preferably between 750 and 1050°C for the cracking tube, for a time of between 0.5 and 12 hours, preferably between 1 and 6 hours.

The silicon compounds which can be used in the process according to the invention can comprise one
20 or more silicon atoms and be inorganic or organic in nature.

Mention may more particularly be made, as inorganic silicon compounds, of silicon halides, hydroxides and oxides, silicic acids, and the alkali
25 metal salts of these acids. Preference is given, among inorganic silicon compounds, to those which do not comprise halogens.

Organic silicon compounds comprising heteroatoms, such as halogen, nitrogen or phosphorus atoms, can also be used. Mention may be made, as
20 examples of such compounds, of chlorotriethylsilane, (3-aminopropyl)triethoxysilane and hexamethyldisilazane.

Mention may be made, as sulphur compounds which can be used in the context of the present invention, of carbon disulphide and the compounds corresponding to the following general formula:



in which R^1 and R^2 , which are identical or different,
each represent a hydrogen atom or a hydrocarbonaceous
5 group and x is a number greater than or equal to 1.
Mention may be made, as examples of hydrocarbonaceous
groups, of alkyl, alkenyl, cycloalkyl or aryl groups
and their combinations, such as, for example, alkylaryl
groups. Mention may more particularly be made, as non-
10 limiting examples of organic sulphur compounds, of
alkyl mercaptans, dialkyl sulphides, dialkyl
disulphides and dialkyl polysulphides, and sulphur
compounds present in some petroleum cuts (naphtha),
such as thiophene and benzothiophene compounds. Use is
15 preferably made of dimethyl sulphide, diethyl sulphide,
hydrogen sulphide and in particular dimethyl
disulphide.

The atomic ratio (Si:S) defining the
proportions of the sulphur compound(s) to the silyl
20 compound(s) is preferably between 5:1 and 1:5. Use is
advantageously made of an Si:S ratio of between 2:1 and
1:2.

The concentration of the additive formed by
the mixture of the sulphur compound or compounds and of
25 the silyl compound or compounds can range from 50 to
5000 ppm by mass in the carrier fluid formed by steam
alone or steam mixed with an inert gas (nitrogen,

The pressure of the carrier fluid is generally equal to that employed conventionally in cracking furnaces (between 1 and 20 bar absolute, advantageously between 1 and 5 bar absolute).

Another subject-matter of the invention is a cracking process in which a sulphur compound and, optionally, a silyl compound is added during the cracking to the feedstock of organic compounds. The temperature at which this addition takes place depends directly on the cracking conditions; it generally varies between 400 and 1000°C and is preferably in 700 and 950°C.

The sulphur compounds and, optionally, the silicon compounds to be used in the context of this embodiment are the same as those mentioned above. The sulphur compound can be used alone or as a mixture with a silyl compound in an Si:S atomic ratio of less than or equal to 2:1, preferably of less than or equal to 1:2.

25 When the organic compound to be cracked
already comprises sulphur in the organic form, only the
silyl compound may optionally be added. In this case,

an Si:S atomic proportion of less than or equal to 2:1, preferably of less than or equal to 1:2, has to be observed, it being necessary for the concentration of silicon in the compound to be cracked not to exceed
5 500 ppm.

The concentration of sulphur additive, with or without silyl compound, is chosen so that the concentration of sulphur in the organic compound to be cracked is between 10 and 1000 ppm by mass, preferably
10 between 20 and 300 ppm by mass.

The following examples illustrate the invention without limiting it.

EXAMPLE 1

This example shows the effectiveness of a
15 pretreatment based on sulphur and on silicon diluted in steam in inhibiting the formation of coke during the cracking of a petroleum cut which is rich in n-hexane (composition given in the following Table 1).

20 **Table 1: Composition of the feedstock to be cracked**

Constituent	% w/w
Cyclopentane	0.23
2,3-Dimethylbutane	1.73
2-Methylpentane	15.70
3-Methylpentane	14.75
n-Hexane	52.28
Methylcyclopentane	12.30
2,4-Dimethylcyclopentane	0.22
Cycloheptane	2.79

The cracking tube, with an internal diameter of 9 mm and a length of 4.6 m, was composed of Incoloy 800 HT steel and had an additional length of 1.45 m of the same tube for the preheating of the fluids.

5 During the pretreatment of the cracking tube, 1.92 kg/h of steam were introduced while maintaining an outlet temperature of the tube of 850°C. The additive is a mixture of dimethyl disulphide and of hexamethyldisiloxane exhibiting an Si:S atomic ratio of
10 2:1. This mixture, diluted in a nitrogen flow of 30 g/h, was injected into the steam after the preheating section at the rate of 5.7 g of additive per hour for 60 minutes. The concentration of additive in the steam was 2970 ppm by mass.

15 The cracking conditions were as follows:

- outlet temperature of the gases 850°C
- pressure 1.7 bar
- contact time 260 ms
- throughput of the feedstock to
 be cracked 4.8 kg/h
- throughput of steam 1.92 kg/h
- dilution 0.4 kg of steam/kg
 of hydrocarbons
- cracking time 6 hours

The decoking of the reactor was carried out by means of a mixture of air (1.2 kg/h) and of steam (4.5 kg/h) brought to 800°C and then 900°C in order to

completely oxidize the coke to carbon oxides. The concentrations of carbon oxides were continually measured by an infrared detector. A portion of the coke which detaches was entrained by the gas flow and then
5 trapped by a cyclone. The mass of coke initially formed in the cracking tube is given by the sum of the coke which has been entrained and of the coke which has been oxidized.

A reference test was carried out under the
10 same conditions (pretreatment, coking and decoking) but without addition of the dimethyl disulphide/hexamethyldisiloxane mixture.

By comparison with this reference test, the mass of coke was found to be reduced by 66% when the
15 tube was pretreated with the dimethyl disulphide/hexamethyldisiloxane mixture.

EXAMPLE 2

This example shows the effectiveness of a pretreatment based on sulphur and on silicon diluted in
20 steam in inhibiting the formation of coke during the cracking of propane.

The cracking tube was composed of Incoloy 800 HT steel with an internal diameter of 7.7 mm and a length of 9 metres. The gases were preheated to 200°C
25 before being introduced into the cracking tube.

The pretreatment used a mixed flow of steam (0.7 kg/h) and of nitrogen (3.5 kg/h) for 4 hours. The

temperature of the gases at the outlet of the cracking tube was 1010°C. The additive was a mixture of dimethyl disulphide and of hexamethyldisiloxane exhibiting an Si:S atomic ratio of 1:2. This additive was injected at
5 the inlet of the pyrolysis tube at the rate of 5.63 g/h, i.e. a concentration of 1340 ppm by mass in the gas flow.

The cracking conditions were as follows:

- outlet temperature of the gases 910°C
- pressure 1.4 bar
- contact time 150 ms
- throughput of the feedstock to be cracked 2.33 kg/h
- throughput of steam 0.7 kg/h
- dilution 0.3 kg of steam/kg of propane
- conversion of the propane 88-92%
- selectivity for ethylene 73-77%
- selectivity for propylene 23-27%
- cracking time 20 hours

The decoking was carried out by means of air
10 (240 g/h) diluted in nitrogen (1.2 kg/h) at a temperature of between 900 and 1000°C. The concentrations of carbon oxides were continually measured by an infrared detector. Coke entrainment phenomena were negligible, which made it possible to

directly calculate the mass of coke formed from the total amounts of carbon oxides.

A reference test was carried out under strictly identical conditions but without addition of
5 the additive based on dimethyl disulphide and on hexamethyldisiloxane.

By comparison with this reference test, the mass of coke was found to be reduced by 27% when the tube was pretreated with the dimethyl disulphide/hexa-
10 methyldisiloxane mixture.

EXAMPLE 3

This example shows the coke-inhibiting properties of a pretreatment based on sulphur and on silicon diluted in steam combined with a continuous
15 addition of dimethyl disulphide to the feedstock.

The general experimental conditions and those of the pretreatment were identical to those of Example 2. The dimethyl disulphide was injected at the inlet of the cracking tube at the rate of 1.8 g/h for
20 the 20 hours during which the cracking of the propane lasted.

A reference test was carried out under identical conditions but without the addition of the pretreatment additive based on dimethyl disulphide and
25 on hexamethyldisiloxane.

By comparison with this reference test, the mass of coke was found to be reduced by 18% when the

tube was pretreated with a dimethyl disulphide/hexamethyldisiloxane mixture.

EXAMPLE 4

This example shows the coke-inhibiting
 5 properties of a pretreatment based on sulphur and on
 silicon diluted in steam combined with a continuous
 addition to the feedstock of a dimethyl
 disulphide/hexamethyldisiloxane mixture.

The general experimental conditions and those
 10 of pretreatment were identical to those of Example 2.
 An additive composed of dimethyl disulphide and of
 hexamethyldisiloxane exhibiting an Si:S atomic ratio
 equal to 1:20 was injected at the inlet of the cracking
 tube at the rate of 1.88 g/h for the 20 hours during
 15 which the cracking of the propane lasted.

A reference test was carried out under
 identical conditions but without additions of the
 pretreatment additive and of the silyl compound during
 the cracking.

20 By comparison with this reference test, the
 mass of coke was found to be reduced by 17%.

COMPARATIVE EXAMPLE 5

The coke-inhibiting properties of a
 pretreatment based on an organic silicon compound alone
 25 (hexamethyldisiloxane) were compared with those of a
 pretreatment without addition of hexamethyldisiloxane.

The general experimental conditions were identical to those of Example 2 but using, as additive, hexamethyldisiloxane injected at the inlet of the cracking tube at the rate of 2.3 g/h during the 4 hours
5 of pretreatment.

By comparison with a reference test carried out under strictly identical conditions but without addition of hexamethyldisiloxane, the mass of coke increased by 5% in the tube pretreated with
10 hexamethyldisiloxane.

EXAMPLE 6

This example shows the effectiveness of a pretreatment by means of an additive based on sulphur and on silicon diluted in steam in inhibiting the
15 formation of coke in a heat exchanger.

Equipment and operating conditions

The micropilot plant was divided into two parts, a cracking reactor followed by a heat exchanger. A small length of metal (carbon steel of P-22 type
20 comprising 2.25% of chromium and 1.0% of molybdenum) was placed in the gas flow passing through this heat exchanger. The coking reactions took place on the surface of this length of metal, resulting in an increase in its mass which could be translated into
25 rate of coking per unit of surface area.

The pretreatment conditions were as follows:

- temperature of the cracking reactor : 600°C

- contact time of the cracking reactor : 2 seconds
- throughput of steam : 21 l/h
- throughput of nitrogen : 7 l/h
- concentration of additive : 1000 ppm
- 5 - temperature of the heat exchanger : 600°C
- duration : 2 hours

The additive based on sulphur and on silicon was a mixture of dimethyl disulphide and of hexamethyl-disiloxane exhibiting an Si:S atomic ratio of 2:1. This
 10 additive was injected into the steam flow at the inlet of the cracking reactor.

The cracking conditions (coking phase) were as follows:

- temperature of the cracking reactor : 850°C
- 15 - contact time of the cracking reactor : 0.5 second
- hydrocarbon to be cracked : isobutane
- throughput of isobutane : 10 l/h
- throughput of nitrogen : 10 l/h
- severity of the cracking
- 20 (propylene/ethylene) : 0.6
- temperature of the heat exchanger : 500°C
- duration : 1 hour

The coke formed in the cracking reactor and the heat exchanger was removed (decoking) by treatment
 25 with air at high temperature in order to convert the carbon into gaseous carbon oxides.

After the pretreatment by means of the additive based on sulphur and on silicon, a coking/decoking cycle was applied in order to obtain a length of metal exhibiting a worn metal surface, representative of the heat exchangers used on industrial units. After this preliminary treatment, the anticoke properties generated by the sulphur-silicon pretreatment and their stability were tested during coking/decoking cycles.

The rates of coking observed on the length of metal placed in the heat exchanger, under standard cracking conditions, during each coking phase are shown in the following Table 2. The rates of coking of the length of metal pretreated with the additive based on sulphur and on silicon are compared with the rates of coking obtained under the same conditions on a length of metal of the same nature but which has not been subjected to any pretreatment.

$$\frac{\begin{array}{l} \text{"Inhibition} \\ \text{of the coke"} \\ (\%) \end{array} = \frac{\begin{array}{l} (\text{Rate of coking on} \\ \text{a length of metal} \\ \text{which has not been} \\ \text{pretreated}) \end{array} - \begin{array}{l} (\text{Rate of coking} \\ \text{on a length of metal} \\ \text{pretreated with S-Si}) \end{array}}{\begin{array}{l} (\text{Rate of coking on} \\ \text{a length of metal} \\ \text{which has not been} \\ \text{pretreated}) \end{array}} \times 100$$

Table 2

Rates of coking of lengths of metal
placed in the heat exchanger

5

	Rates of coking ($\mu\text{g} \times \text{cm}^{-2} \times \text{min}^{-1}$)		Inhibition of the coke (%)
	Untreated length of metal	Length of metal treated with S and Si	
Cycle 1	42	17	59
Cycle 2	54	23	57
Cycle 3	66	31	53
Cycle 4	84	38	55
Cycle 5	90	52	42
Cycle 6	100	64	36

25 6. Process according to one of Claims 1
to 5, in which use is made, as silyl compound, of a

compound comprising only silicon, carbon, hydrogen and, optionally, oxygen.

7. Process according to Claim 6, in which the silyl compound is hexamethyldisiloxane.

5 8. Process according to one of Claims 1 to 7, in which use is made, as sulphur compound, of carbon disulphide or a compound of general formula $R^1-S_x-R^2$ in which R^1 and R^2 , which are identical or different, each represent a hydrogen atom or a
10 hydrocarbonaceous group and x [lacuna] a number equal to or greater than 1.

9. Process according to Claim 8, in which the sulphur compound is dimethyl disulphide.

10. Process according to one of Claims 1
15 to 9, in which the Si:S atomic ratio is between 5:1 and 1:5, preferably between 2:1 and 1:2.

11. Process according to one of Claims 1 to 10, in which the concentration by mass of sulphur and silyl additives in the carrier fluid is between 50
20 and 5000 ppm, preferably between 100 and 3000 ppm.

12. Process according to one of Claims 1 to 11, in which the pressure varies between 1 and 20 bar absolute, preferably between 1 and 5 bar absolute.

13. Process according to one of Claims 1
25 to 12, in which, after the pretreatment, a sulphur compound and/or a silyl compound are added to the feedstock of the organic compound to be cracked.

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(54) Title: COKING REDUCTION IN CRACKING REACTORS

(54) Titre: REDUCTION DU COKAGE DANS LES REACTEURS DE CRAQUAGE

(57) Abstract: The invention concerns a method for reducing coking on the metal walls of a reactor cracking hydrocarbons or other organic compounds and on the metal walls of a heat exchanger placed downstream of the cracking reactor, whereby the metal surfaces coming into contact with the organic substance to be cracked are pre-treated with a water vapour stream containing at least silicon and at least a sulphur compound.

(57) Abrégé: Pour réduire le cokage sur les parois métalliques d'un réacteur de craquage d'hydrocarbures ou d'autres composés organiques et sur les parois métalliques d'un échangeur thermique placé à la suite du réacteur de craquage, les surfaces métalliques venant en contact avec la substance organique à craquer sont prétraitées avec un courant de vapeur d'eau contenant au moins un composé du silicium et au moins un composé du soufre.

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Convention & Non-convention
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(check one) ☐ is attached hereto.

☒ was filed as U.S. Application No. _____ on 22 March 2002 and (if applicable) was amended on 22
March 2002

☒ was filed as PCT International Application No. PCT/FR00/02583 on September 18, 2000 and (if applicable) was amended under PCT Article 34 on _____.

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign and PCT application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration. I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed.

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99/11965 ✓	FRANCE ✓	September 24, 1999 ✓	YES

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U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

The duty is acknowledged for the Preliminary Amendment, which is hereby incorporated by reference as part of the original disclosure.

I hereby claim priority benefits under Title 35 United States Code §119(e) of any U.S. provisional application(s) listed below.

U.S. Provisional Application No.	Filing Date

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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☒ Additional inventors and/or prior applications are listed in attached Supplemental Sheet(s).

